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EXECUTIVE SUMMARY OF THE THESIS

Investigation on the effect of Benzoyl Peroxide on the synthesis of polyynes via Pulsed Laser Ablation in Liquid

LAUREA MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY - INGEGNERIA DEI MATERIALI E DELLE NANOTECNOLOGIE

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1. Introduction

Polyynes are linear sp-carbon chains characterized by the alternation of single and triple bonds [1]. In the last decades, polyynes have been successfully synthesized through several chemical and physical methods. Indeed, many research groups have employed physical methods for the synthesis of polyynes, due to the possibility of industrial scale-up and their lower cost [1, 2]. Pulsed Laser Ablation in Liquid (PLAL) is a physical technique based on the action of a pulsed laser on a target immersed in a liquid phase [2]. The laser beam has a high energy density and it generates a plasma when hits the target surface. Thus, fragments and atoms of the target are detached from the surface [3]. Carbon atoms in the plasma plume form polyynes through the subsequent addition of C₂ or C radicals, building up the chains [4]. This polymerization process competes with termination processes occurring through the addition of end-groups, such as hydrogenation [4]. Several PLAL parameters were shown to influence the production of polyynes, however few works are present in literature regarding the use of solute compounds [2, 5]. Since the mecha-

nism of growth of polyynes is supposed to involve radical clusters, I investigated the effect of a radical initiator (Benzoyl Peroxide - BPO) on the synthesis of polyynes via PLAL. In this way I wanted to investigate the parameters that govern the chain growth and the termination, trying to obtaining more concentrated and longer chains. Moreover, by employing Benzoyl Peroxide I tried to understand the effect of reactive molecules on the synthesis of CAWs.

2. Materials and Experimental Methods

In all my experiments, I synthesized polyynes via PLAL ablating a graphite target with a purity of 99.99% (Testbourne Ltd). I employed a Nd:YAG pulsed laser (Quantel Q-Smart 850) with a repetition rate of 10 Hz and a pulse duration of 6 ns, and I used the three available harmonics (1064 nm, 532 nm and 355 nm). All the performed ablations employed a fluence of 2.71 J/cm² and 5 ml of solution. As solvents, methanol (MeOH), ethanol (EtOH), isopropylalcohol (IPA) and acetonitrile (ACN) were employed (HPLC grade, purity $\geq 99.9\%$, Sigma-

Aldrich). Regarding BPO, Luperox[®]A75 was used, which is 75% crystalline BPO in powder form. 5 mM solution of BPO were prepared in all the solvents, while with IPA I prepared BPO solutions with increasing concentrations in the 0.02 mM-10 mM range. 15 min ablations were performed in all solutions, while in IPA I ablated also for 30 min and 120 min.

Reverse-phase high-performance liquid chromatography (RP-HPLC) was employed to detect and separate each polyynes. A Shimadzu Prominence UFLC was employed, equipped with a photodiode array detector (DAD) UV-Vis spectrometer (with a range from 190 nm to 800 nm) and a FRC-10A fraction collector. In this thesis work, I mainly employed a C18 LC column (Phenomenex Luna[®] C18, 150 mm × 4.6 mm, 3 μm particle size). Each ablated solution was first filtered using Phenomenex Phenex RC membrane syringe filters having a pore size of 0.45 μm in order to remove any carbon particulate and other impurities that might obstruct or damage the columns. The majority of the ablations were analysed using a gradient method on the Luna[®] C18: this method involved a mobile phase of acetonitrile and water, after 4 minutes of constant ACN concentration, the percentage of ACN was increased linearly from 65% to 95%, reaching the final value at 20 min, then the concentration was kept constant until the end at 45 min. The flow rate of the mobile phase was 0.800 mL/min. A small volume of 15 μL was taken from each ablation and injected

in the HPLC to be analysed, however the injection volume was reduced when dealing with solutions with BPO concentration of 7.5 mM and 10 mM, in these two cases the injection volume was reduced to 10 μL and 7 μL respectively. This method was chosen since allows to well separate the chromatographic peaks of all polyynes, including methyl- and cyano-capped, with chains length up to 22 carbon atoms.

3. Experimental Results

3.1. Effect of BPO in IPA

The total concentration of synthesized polyynes from the ablations at 532 nm in solutions of IPA with increasing concentrations of BPO are reported in Fig. 1. Increasing the BPO concentration corresponds to an increase in the mean polyynes concentration. In pure IPA the average concentration of polyynes is shown to be $(5.1 \pm 0.4) \times 10^{-5}$ mol/l. Instead, in the solutions with 5 mM of BPO a mean total concentration of $(7.2 \pm 0.2) \times 10^{-5}$ mol/l was obtained, which corresponds to a ratio between the polyynes concentration in 5 mM BPO solutions over the concentration in pure IPA of 1.4 ± 0.1 . The maximum concentration of polyynes was obtained by ablating 7.5 mM solutions, reaching an average value of $(7.72 \pm 0.06) \times 10^{-5}$ mol/l, which corresponds to a ratio of 1.5 ± 0.1 . The same set of solutions was ablated also at 1064 nm. Also in this case, a general increase in the synthesis yield of polyynes was visible, though lower than with 532 nm. The mean ratio between polyynes concentration in BPO solution and pure IPA was relevant for concentrations of BPO above 5 mM. For 5 mM and 7.5 mM the ratio were 1.18 ± 0.09 and 1.2 ± 0.1 respectively, while the maximum increase in the synthesis yield was reached for 10 mM solutions, with a ratio of 1.3 ± 0.1 . Hence, the solutions with BPO had a higher production of polyynes for both wavelength at 15 min, however the highest increase in the synthesis yield was obtained at 532 nm. Moreover, the concentration of polyynes seems to be dependent on the concentration of BPO in solution. Indeed, for 532 nm a clear increasing trend is shown by increasing the concentration of BPO (see Fig. 1).

The presence of BPO was also shown to have a greater effect on longer polyynes than shorter

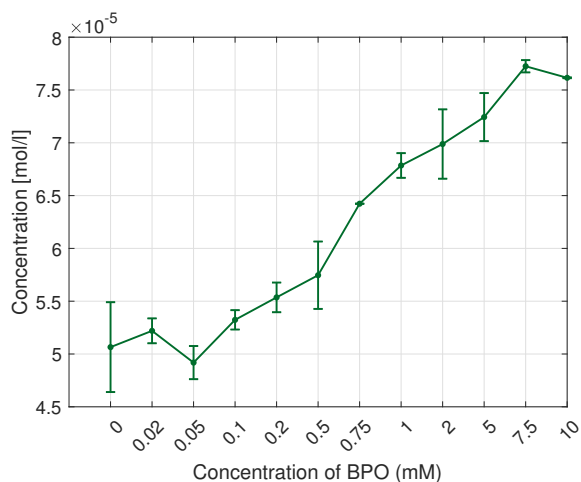


Figure 1: Concentration of all polyynes produced, regardless of the length, by ablations in IPA with increasing concentration of BPO at 532 nm for 15 min.

ones. As for the total concentration, I calculated the ratio of the concentration of each size-selected polyynes in the solutions with BPO over the concentration of the same polyynes in pure IPA. The ratio of C_6 , C_{14} and C_{20} (hydrogen-capped) are reported in Fig. 2. As shown by Fig.

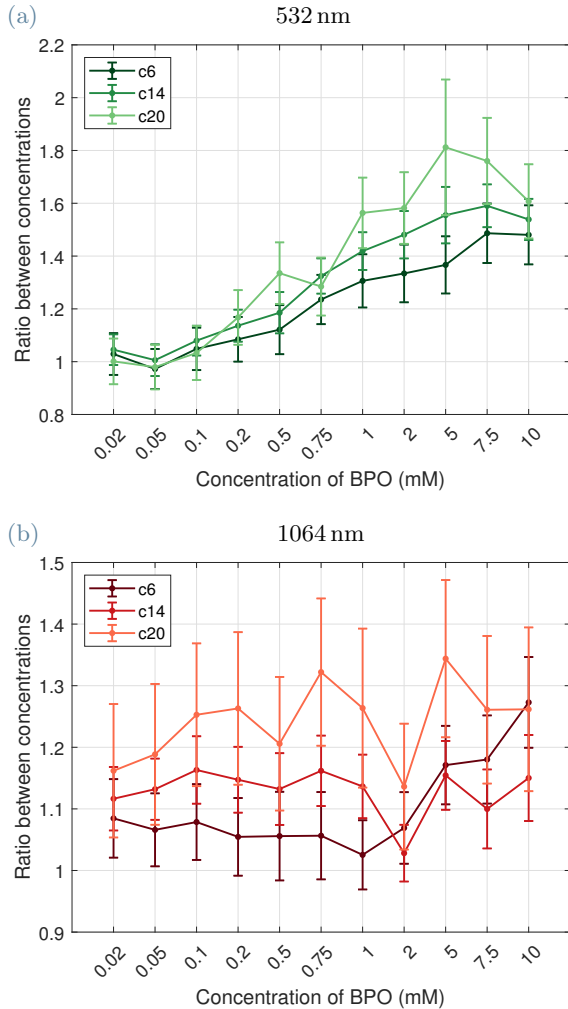


Figure 2: Ratios between the concentrations of size-selected hydrogen-capped polyynes produce in BPO solutions over those in pure IPA for ablations performed for 15 min at (a) 532 nm and (b) 1064 nm. Three size-selected polyynes are displayed, namely C_6 , C_{14} and C_{20} .

2a, for 532 nm the presence of BPO leads to different increases depending on the chain length, the synthesis yield of longer polyynes was increased more than that of shorter ones. Hence, in agreement with the results on total polyynes concentrations, an increase in BPO concentration corresponded to an increase in the concentration of each size-selected polyynes. Furthermore, the relative amount of longer polyynes was increased with respect to the shorter ones by

ablating in BPO solutions. Regarding the ablations performed at 1064 nm, the synthesis yield of longer chains was increased more than that of shorter ones, as shown by the graph in Fig. 2b. However, the increase was less significant compared to the ablations at 532 nm. Shorter chains as C_6 have ratios between 1 and 1.1, and only for the most concentrated BPO solutions a higher increase was recorded. Longer chains have slightly higher ratios. The increase ratio of C_{14} oscillates around 1.1. C_{20} had a bigger increase around 20%, irrespective of the concentration of BPO.

A similar effect was reported for methyl-capped polyynes, indeed the same trend of hydrogen-capped polyynes was recorded also for methyl-capped polyynes, when ablating BPO solutions at 532 nm. A clear gain in the concentration of methyl-capped polyynes is shown for the 1 mM, 2 mM, 5 mM, 7.5 mM and 10 mM solutions, and longer chains were more favoured by the presence of BPO. The maximum concentrations were achieved for ablations in 7.5 mM, reaching an increase at around 60% for $C_{16}CH_3$ (methyl-capped) (with a ratio of 1.6 ± 0.1). Regarding the ablations at 1064 nm, the effect of BPO does not show a clear trend. For shorter chains an increase in the synthesis yield was always recorded, though small and relevant only for concentrations of BPO above 5 mM. In the latter solution, $C_{10}CH_3$ achieved a ratio of 1.22 ± 0.05 . However, longer chains showed a decrease in their synthesis efficiency at high BPO concentrations, with concentrations smaller than that of pure IPA (i.e. ratios smaller than 1).

3.2. Effect of laser wavelength in pure IPA

Ablations in pure IPA were performed with 1064 nm, 532 nm and 355 nm and the concentration of each polyynes was recorded. Ablations performed at 1064 nm produced higher concentrations of each size-selected polyynes with respect to 532 nm and 355 nm, whose production was the lowest. For example, C_6 hydrogen-capped polyynes was produced in concentration of $(2.8 \pm 0.1) \times 10^{-5}$ mol/l via ablations at 1064 nm, while the concentration was $(2.3 \pm 0.2) \times 10^{-5}$ mol/l at 532 nm and $(1.28 \pm 0.05) \times 10^{-5}$ mol/l at 355 nm. Hence, longer laser wavelengths correspond to higher concentrations of

polyynes, when ablating a solid graphite target in pure IPA. This result was obtained both for hydrogen-capped and methyl-capped polyynes. Moreover, longer chains were also favoured by longer laser wavelength. Indeed, the concentration of C_{20} in ablations at 1064 nm was five times larger than in ablations at 532 nm, while C_{22} in ablations at 1064 nm was an order of magnitude larger than at 532 nm. This was true also for methyl-capped polyynes. In 1064 nm ablations I detected chains with length up to $C_{20}CH_3$ with a mean concentration of $(1.13 \pm 0.07) \times 10^{-8}$ mol/l, while in 532 nm $C_{18}CH_3$ was barely detectable with a concentration around 6×10^{-9} mol/l.

3.3. Effect of ablation time

5 mM BPO solutions and pure IPA were also ablated for longer times: 30 min and 120 min. By ablating pure IPA, an overall increase in the concentration of polyynes was recorded for both ablation times with respect to 15 min and the maximum concentration was reached for 120 min. Hence, the total concentration of polyynes increases as the ablation time increases in pure solvent ablations, irrespective of the wavelength employed. However, the change in the synthesis yield was not the same for each chain length: indeed, for ablation at 532 nm and 120 min, shorter chains were favoured, while longer chains, as C_{20} and C_{22} , were less concentrated than at 15 min. This effect could be related to photofragmentation phenomena induced in longer chains by 532 nm laser light. Therefore, though the increase in the ablation time, 532 nm does not allow to synthesize a significant amount of polyynes longer than C_{22} . On the contrary, I did not record this effect for 1064 nm, for which the concentration of each polyyne was increased. The same effect was also recorded for methyl-capped polyynes.

Regarding the effect of BPO, in Fig. 3 the ratio between the concentrations of each size-selected polyyne in 5 mM solutions over pure IPA are reported for both wavelength. The effect of BPO in ablations of 30 min (Fig. 3a) seems to be similar to the results at 15 min, with a bigger gain for ablations performed with the 532 nm laser. However, by further increasing the ablation time to 120 min a larger increase was obtained for 1064 nm, while for 532 nm the ablations in 5 mM BPO solutions showed a lower production than

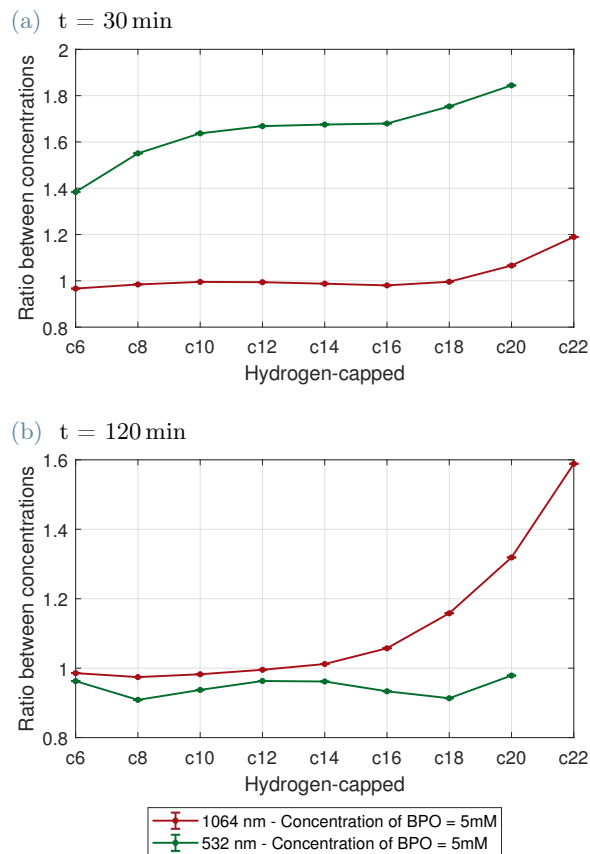


Figure 3: Ratio between the concentrations of size-selected hydrogen-capped polyynes in 5 mM BPO solutions and those in pure IPA for ablations performed at 1064 nm (red line) and 532 nm (green line) for (a) 30 min and (b) 120 min.

in pure IPA (see Fig. 3b). This result suggests the presence of different processes occurring during the ablations with different laser wavelength. However, this effect is still under investigation. For methyl-capped polyynes the effect of ablation time on BPO was the same. Moreover, I analysed the ablations at 30 min and 120 min in pure IPA and with BPO with another chromatographic method, and I managed to identify C_{24} and C_{26} polyynes.

3.4. Mechanism of BPO

In the chromatograms of the solutions with BPO a broad band containing the degradation products of BPO was detected. From the absorption spectra I suppose this compounds were benzoic acid (BA), methyl benzoate (MeBA) and ethyl benzoate (EtBA). This implies that some percentage of BPO was reacting through the cleavage of the O–O bond, by thermal or photo-induced activation. Benzoate radicals, i.e. the

products of the cleavage of the O–O bond, need hydrogen atoms to form benzoic acid and in PLAL experiments the only source of hydrogen atoms was the solvent. In the PLAL process, the plasma generated by the laser atomizes the solvent molecules, thus a source of free hydrogen atoms is the plasma plume. Hence, BPO molecules close to the plasma should have a higher probability to react and capturing H-atoms or other fragments, thus forming degradation products. This process may induce a depletion region of endgroups around the plasma favouring the polymerization of polyynes at the expense of hydrogenation and termination processes. For these reasons, I observed experimentally an increase in the overall polyyne concentration and, in particular, this mechanism can favour the formation of longer polyynes. Indeed, since the termination reactions are less probable, the polymerization process allows the chains to grow longer. This hypothesis explains the presence of degradation products and the higher concentration of polyynes. An increase in the BPO concentration corresponds to a higher concentration of benzoate radicals around the plasma plume, and hence to a greater depletion of hydrogen atoms. Therefore, higher concentrations of BPO produce more and longer polyynes as shown by the results. However, the effect of different wavelengths is not clear, and could be related to the presence of further mechanism. For example, processes of ring-opening of the two phenyl groups in BPO could increase the production providing larger radicals. This phenomenon could be favoured by 532 nm due to more energetic photons. However, this process should not form BA as degradation product since the BPO molecules would be destroyed. 1064 nm photons could instead excite vibrational mode of the BPO molecules, hence increasing the probability of the radical activation of BPO.

3.5. Effect of BPO in other solvents

Similar results were obtained for methanol and ethanol for ablations in 5 mM BPO solutions, as shown in Fig. 4. The main effect that emerges from these graphs is that ablations in BPO solutions produced more polyynes than in pure solvents. As for IPA, 532 nm led to a higher gain in the synthesis yield of polyynes than 1064 nm

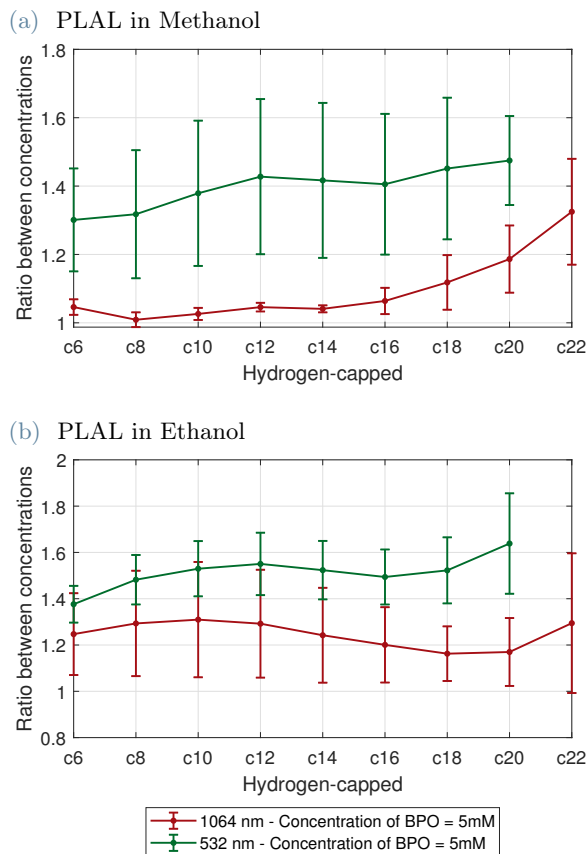


Figure 4: Ratio between concentrations of size-selected hydrogen-capped polyynes in 5 mM solutions over those of the same polyyne in pure (a) methanol and (b) ethanol, for both ablation wavelengths (1064 nm, red line, 532 nm, green line).

for both alcohols. Considering only the ablations with 532 nm, ablations of BPO solutions in IPA showed the highest ratios followed by EtOH and then MeOH. Considering ablations with the 1064 nm laser, they showed smaller gains in the polyyne concentrations compared to 532 nm as observed in IPA. The effect of BPO, also in these cases, seems to be more relevant on longer chains, however the gains for both MeOH and EtOH are smaller compared to IPA. Indeed, the average ratio of C_{20} with 532 nm for MeOH is 1.5 ± 0.1 , for EtOH is 1.6 ± 0.2 compared with 1.8 ± 0.3 of IPA. With 1064 nm the ratios of shorter chains in MeOH are close to the unity with small increase in concentrations, but they increases significantly for C_{18} , C_{20} and C_{22} reaching 1.3 ± 0.2 for C_{22} . On the contrary, for EtOH 1064 nm ablations in BPO solutions produced higher gains with respect to MeOH and the ratios oscillate around 1.2 for all the chains. Acetonitrile instead showed a different be-

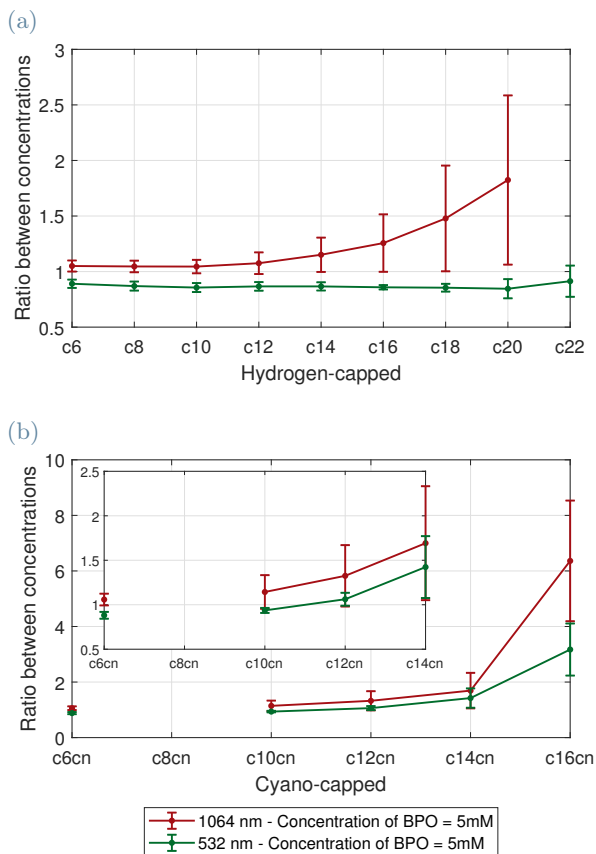


Figure 5: Ratio between the concentrations of size-selected (a) hydrogen- and (b) cyano-capped polyynes in 5 mM BPO solutions and that of the same polyynes in pure ACN for ablation of 15 min with 1064 nm (red line) and 532 nm (green line) laser light. The inset in Fig. (b) shows the zoomed area between C₆CN and C₁₄CN.

behaviour. The result for hydrogen-capped polyynes is shown in Fig. 5a. As it is clearly shown by the graph, the concentration of polyynes in 532 nm ablations was lower than in pure ACN, while in 1064 nm ablations an increase was visible, though small. Only longer chains in 1064 nm ablations had larger gains, although C₁₈ and C₂₀ ratios are affected by large error bars due to the high variability of the ablations in ACN. An interesting result was shown for cyano-capped polyynes instead. For both wavelengths long cyano-capped polyynes were favoured (see Fig. 5b). Indeed, the concentration 16-atoms cyano-capped polyynes (C₁₆CN) was found to be 310% of the concentration in pure acetonitrile for 532 nm ablations and even larger (up to 600%) for 1064 nm.

4. Conclusions

It was shown that Benzoyl Peroxide contributes to the synthesis of polyynes, increasing the concentration of hydrogen-capped and methyl-capped polyynes in conjunction with several parameters. In BPO and IPA solutions an increase in the concentration of each hydrogen-capped polyynes was obtained with respect to the pure solvent. The gain in the concentration was shown also to be dependent on the concentration of BPO in the solution. More concentrated BPO solutions corresponded to higher gain with respect to pure IPA. The effect of BPO was shown to be more favoured by 532 nm laser rather than 1064 nm, when ablating for 15 min. A similar result was also obtained for methanol and ethanol. However this was not true for acetonitrile, which exhibits a different behaviour. Also cyano-capped polyynes showed to be increased by the presence of BPO.

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